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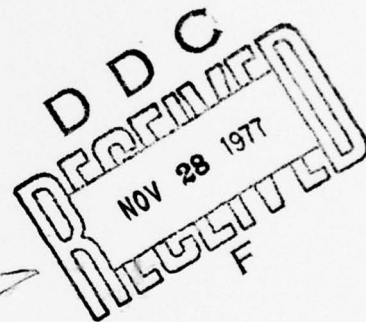Project No. NR 092-556

ANNUAL SUMMARY REPORT

"HIGH SPEED ELECTRON SPIN RESONANCE STUDIES

OF FREE RADICALS IN STRESSED POLYMERS"

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

It has been known for some time that mechanical stressing of a polymer is accompanied by bond rupture. The number of bonds ruptured is dependent on the sample morphology, the method of mechanical degradation, and the temperature relative to T_g. If a sufficient number of bonds rupture, the free radicals thus formed are detectable using electron spin resonance (ESR) techniques.

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The information which has been uncovered in the extensive ESR studies of polymer fracture is outlined. Employment of microsecond response time ESR instrumentation is proposed for characterizing the sequence of radical reactions triggered by polymer fracture above cryogenic temperatures.

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"High Speed Electron Spin Resonance Studies
of Free Radicals in Stressed Polymers"*

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Abstract

It has been known for some time that mechanical stressing
of a polymer is accompanied by bond rupture. The number of bonds
ruptured is dependent on the sample morphology, the method of
mechanical degradation, and the temperature relative to T_g. If a
sufficient number of bonds rupture, the free radicals thus formed
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The information which has been uncovered in the extensive
ESR studies of polymer fracture is outlined. Employment of micro-
second response time ESR instrumentation is proposed for charac-
terizing the sequence of radical reactions triggered by polymer
fracture above cryogenic temperatures.

Introduction

Free radical formation from mechanical stressing of polymers was first reported in 1959 by Bresler et al. (1), and Butyagin et al. (2). They used election spin resonance (ESR) to observe the radicals produced by pulverizing polymers in a mill at liquid nitrogen temperature. Since that time, rather extensive studies of radicals formed by mechanically stressing polymers have been carried out, especially by the groups of Zhurkov and Zakrevskii in the USSR, and DeVries and Peterlin in the USA.

Interestingly, mechanical shearing of a polymer in the presence of a monomer (or of two different polymers) is a synthetic route to block copolymers. The radicals formed by chain scission undergo polymerization and recombination reactions. Although the method requires a large amount of power, and the block lengths and distributions have a certain randomness, unusual product properties can be obtained.

Free Radicals and Fracture Processes

It is thus well established that the macroscopic fracture of polymers is accompanied, in varying degrees, by the rupture of chemical bonds. The number of radicals formed depends on the method of mechanical degradation, the nature of the polymer, and the temperature. Crushing a polymer by milling or grinding, for example, produces a large amount of fracture surface, and hence a relatively large ESR signal. In the case of tensile deformation, large ESR signals are observed only for polymers having high

strengths, such as semi-crystalline polymers with fibrous structure. With regard to temperature, T_g appears to be a key parameter. For example, a fibrous sample stressed at a temperature well above T_g will generate few, if any, detectable radicals; at lower temperature, the radical population is increased; below T_g, the largest number of radicals result.

Temperature also affects the lifetimes of radicals. It was established in some of the early studies that low temperature grinding of a polymer produces chain-end (primary) radicals resulting from main chain scission. If such a sample is warmed after grinding, the ESR signal changes to that of a center of chain (secondary or tertiary) radical. (The chemistry of these processes will be covered in detail below).

On the other hand, if a sample is ground at the higher temperature, the ESR spectrum obtained is that of the center of chain radicals. It has been concluded that although chain-end radicals are the initial radical types produced in the fracture process they are not the radicals observed in the conventional ESR experiment, except at cryogenic temperature where their reactivity is greatly reduced. Rare exceptions to this rule occur in the case of unusually stable chain-end species, which might for example, be resonance stabilized or sterically hindered. Thus, room temperature stressing of poly[p-(2-hydroxyethoxy) benzoic acid] fibers produces long lived primary phenoxy radicals (3).

Fracture of a sample at low temperature in order to trap the initial chain-end radicals is not a satisfactory solution for most polymers unless one resorts to crushing techniques to create large fracture surface area. Otherwise, in a mechanical test such as tensile loading, many engineering polymers are so brittle at low temperature that the samples break before detectable levels of free radicals are formed.

A brittle polymer is a poor candidate for ESR studies in tensile tests because the fracture damage is largely confined to a thin cross-section perpendicular to the direction of applied stress. If complete orientation is assumed, the number of polymer chains passing through a square centimeter of sample cross-section is about 5×10^{14} for a chain cross-section of $20\overset{\circ}{A}^2$. At the most, then, twice this number or 10^{15} radicals/cm^2 could be generated in the fracture surface of a polymer which fails in a brittle mode (4). The radical levels observed in the case of high tenacity fibrous polymers, however, are some 100 to 1000 times larger than this. Furthermore, for fibrous polymers it is well established that chain rupture does not occur within the crystalline blocks, but is confined to tie chains in the amorphous regions, which constitute only a small fraction of the specimen cross-section. Thus, free radical levels of $10^{17}-10^{18}$/cm^2 cannot be accounted for by bond ruptures localized at the macroscopic failure surface. In high tenacity polymers, chain rupture under tensile stress is a bulk, or volume effect that involves the entire specimen.

Applications

An elusive goal of the numerous studies of stress-generated radicals in fibrous polymers is the development of a definitive microscopic model which accounts for both the spectroscopic (ESR, IR, etc.) observations and the details of the fracture mechanism. It is not within the scope of this paper to cover such a topic in any detail. However, it should be mentioned that a good correlation exists between the intensity of the ESR signal and the stress which a particular fibrous sample has experienced. If the same sample is stressed again, virtually no new radicals are formed until the strain limit of the first run is exceeded. One can visualize that the sample strain reached during the previous run has caused the rupture of any chain which bore a load greater than the strength of its weakest link. In the next run, no intact chains remain to be fractured up to the load limit of the previous run. Peterlin (5) has in fact proposed measurement of the free radical signal as the basis of a nondestructive test for assessing the strain level which a sample has experienced.

ESR intensity measurements also may be of utility for the evaluation of filled polymer systems. Elastomers containing different fillers showed varying free radical content when pulled to fracture (6). SEM pictures showed that elastomer adhesion to particles changed from poor to good, corresponding to negligible or large ESR signals, respectively. In the latter cases, chain rupture occurred due to cohesive elastomer fracture. Because of

5

rapid radical decay, the experiments had to be carried out below -60°C, however SEM studies showed little change in appearance of the fracture surface from that obtained at room temperature.
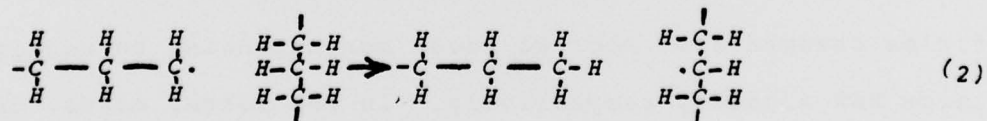
Chemistry of the Radical Processes

Our particular interest in polymer fracture is primarily in the chemical consequences of chain breaking as determined by ESR techniques. It will be useful to examine the radical chemistry aspects of chain breaking before discussing the details of the ESR experiment.

Our model for the polymer chain will be polyethylene. To eliminate competing reactions involving oxygen, moisture, etc., either vacuum or a dry nitrogen blanket is assumed. The initial consequence of chain breaking is the formation of two primary chain-end radicals (eq. 1). At ordinary temperatures, sufficient

$$
-\overset{\underset{H}{|}}{\underset{}{C}}- \quad\quad -\overset{\underset{H}{|}}{\underset{}{C}}-\overset{\underset{H}{|}}{\underset{}{C}}- \longrightarrow -\overset{\underset{H}{|}}{\underset{}{C}}-\overset{\underset{H}{|}}{\underset{}{C}}\cdot \quad \cdot\overset{\underset{H}{|}}{\underset{}{C}}-\overset{\underset{H}{|}}{\underset{}{C}}-\overset{\underset{H}{|}}{\underset{}{C}}- \tag{1}
$$
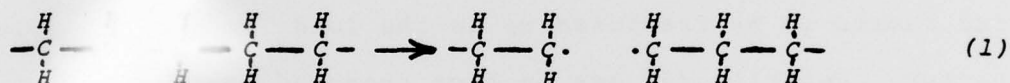
backbone motion exists for the diffusive encounter of the chain-end radicals with neighboring chains, from which hydrogen atoms may be abstracted (eq. 2). Alternatively, an α-hydrogen atom may be eliminated, leaving a vinyl group (eq. 3). This hydrogen atom may scavenge a hydrogen atom from a neighboring polymer chain, forming a hydrogen

$$
-\overset{\underset{H}{|}}{\underset{}{C}}-\overset{\underset{H}{|}}{\underset{}{C}}-\overset{\underset{H}{|}}{\underset{}{C}}\cdot \quad \begin{matrix} H-C-H \\ H-\overset{\cdot}{C}-H \\ H-C-H \end{matrix} \longrightarrow -\overset{\underset{H}{|}}{\underset{}{C}}-\overset{\underset{H}{|}}{\underset{}{C}}-\overset{\underset{H}{|}}{\underset{}{C}}-H \quad \begin{matrix} H-C-H \\ \cdot C-H \\ H-C-H \end{matrix} \tag{2}
$$

molecule and a center of chain radical (eq. 4). The chain-center

6

$$-\overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} \cdot \longrightarrow -\overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{}{C}} = \overset{H}{\underset{H}{C}} + H \cdot \qquad (3)$$

$$H \cdot + \begin{matrix} H-\overset{|}{C}-H \\ H-\overset{|}{C}-H \\ H-\overset{|}{C}-H \\ | \end{matrix} \longrightarrow \begin{matrix} H-\overset{|}{C}-H \\ \cdot C-H \\ H-\overset{|}{C}-H \\ | \end{matrix} + H_2 \qquad (4)$$
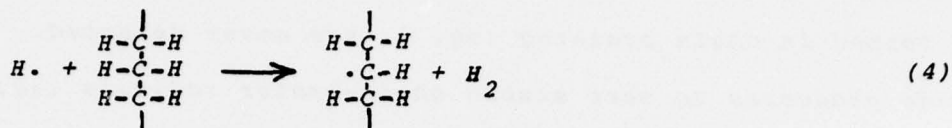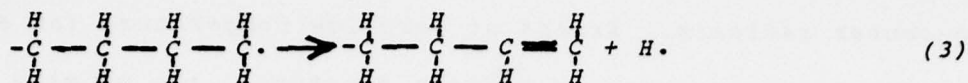
radicals formed (eq. 2,4), constitute weak links in the polymer
backbone, the activation energy for adjacent bond fission being
significantly lower than that for a normal chain (5,7,8). A
terminal vinyl group and a new chain-end radical result from its
rupture (eq. 5). It is to be noted that the reaction shown in

$$-\overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \longrightarrow -\overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} \cdot \quad \overset{H}{\underset{H}{C}} = \overset{H}{\underset{}{C}} - \overset{H}{\underset{H}{C}} - \qquad (5)$$
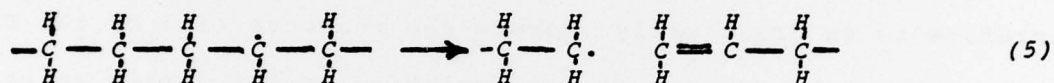
eq. 2-5 do not alter the number of free radicals in the sample from
that generated in the initial chain ruptures. The number of <u>radicals</u>
present remains equal to twice the number of chains ruptured via the
process shown in eq. 1 (primary rupture), neglecting radical recom-
bination reactions. However, the number of <u>chains</u> ruptured by the
process shown in eq. 5, called secondary rupture, can be very large,
and may exceed by a factor of hundreds the number of primary ruptures
(7). ESR, of course, can detect only the species which contain
unpaired electrons; other means have to be employed to determine
vinyl groups, methyl groups, H_2, etc.

Even if we restrict ourselves to considerations of the radi-
cals taking part in eq. 1-5, the information that conventional ESR
can obtain is limited. A conventional ESR spectrometer, with its
response time of seconds to minutes, detects only the long lived

7

chain-center radicals. Except at very low temperature (an environ-
ment which leads to unwanted brittle fracture), the primary radi-
cals formed in chain breaking (eq. 1) are never detected. The
cascade processes to more stable chain-center radicals (eq. 2-4),
and the occurrence of secondary rupture (eq. 5) produce no net
change in the integrated intensity of the ESR signals; furthermore,
the observed ESR line shape is a superposition of lines from the
various stable radicals left after all the chemistry has taken
place.

An alternative to slowing down the chemistry by lowering the
temperature is to drastically improve the response time of the ESR
spectrometer. Accordingly, we have modified an ESR system so that
its response time is of the order of one microsecond (9-11).
Signals are digitized and stored on this time scale. To achieve
fast sweeping of the magnetic field, rapid scan coils and a drive
system were installed (12). The magnetic field can be repetitively
swept in a few milliseconds over a 60 gauss range, while the signal
is sampled at microsecond intervals and digitally stored in a multi-
channel Nicolet signal averager.

Preliminary room temperature experiments have been carried out
on a fiber bundle of research grade nylon 6 (13), using a simple
dead weight tester. Subtraction of ESR spectra taken sequentially
over a time span of approximately one second revealed the transient
existence of a radical whose spectrum is not observed in conven-
tional ESR experiments.

Presently, a programmable servo-controlled tester (4,14) which will interface with our high speed ESR spectrometer is being built at Utah under the direction of Professor DeVries. Professor DeVries and Dr. G. Chingas are collaborating with us in the polymer fracture work. We hope that additional data obtained using the new tester will be available at the time of the review.

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